

Soft X-Ray Spectromicroscopy Investigation of the Formation and Ageing of Eu(III)-induced Humic Acid Aggregates

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Introduction: The role of humic substances (HS) in the context of risk assessment for nuclear waste disposal sites is a subject of intensive research. One central aspect of this research is to evaluate the influence humate phases have on the mobility or retention of actinide cations. Humic substances possess a variety of functional groups which may serve as metal ion binding sites. Previous XAFS studies point to carboxylate groups primarily attaching metal cations. The humate complex stability may change with the number of functional groups involved in metal binding or with the steric conformation assumed by the organic macromolecules.

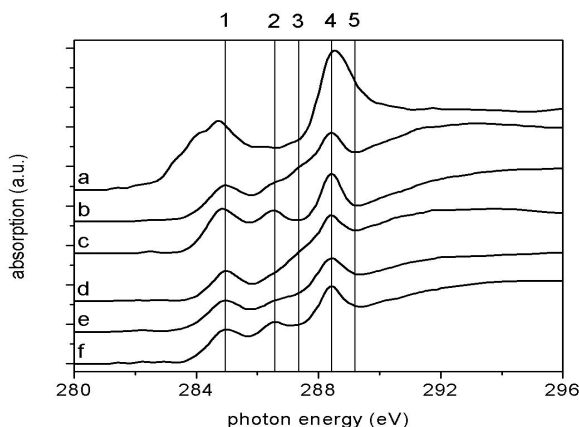
Methods and Materials: A stock solution of 400 mg/L purified Aldrich humic acid (HA) with an electrolyte content of 0.1 mol/L NaCl is adjusted to pH 6.0. The amount of Eu(III) calculated to saturate the total loading capacity of Aldrich HA is added. A 400 mg/L HA concentration chosen in these experiments cannot be studied by spectromicroscopy without loading with Eu(III). It is only possible at reduced pH values, where protonation of functional carbon groups induces the formation of HA colloidal aggregates. Spectromicroscopy investigations are performed at the X-1A outboard-STXM. Thin films of aqueous colloid suspensions are enclosed between silicon nitride membranes.

Results: The STXM micrographs of HA aggregates formed at pH 4.3 reveal a subtle structure with particles and larger sheets of carbonaceous material embedded in a fibrous network. The morphology of these aggregates changes drastically upon addition of Eu(III)-cations, where dark, dense patches of organic material are dispersed in lighter, less dense regions with about one third of optical density. An increase in densification of the Eu(III)-humate aggregates with time is observed over a period of several months. After four weeks, the sharp contrast between the now enlarged dark zones and the less absorbing material remains. Samples aged for 7 months in contact with Eu(III)-cations only exhibit dense zones of partially overlapping sheets of carbon-rich material, with rather uniform thickness. The dramatic HA morphological changes induced by Eu(III)-complexation are reflected in the C 1s-NEXAFS (s. Figure). Beginning with the unloaded HA at pH 4.3, spectrum **a** is dominated by two intense and broad resonances centered around 284 eV and 289 eV. The spectral signature is independent of the region selected in the image of this sample to extract the NEXAFS; only minor intensity variations are observed. In contrast, the dark and light zones in the HA agglomerates formed upon addition of Eu(III) (spectra **b**, **c**) exhibit C 1s-NEXAFS spectra indicating the presence of separated organic species with primarily different absorption intensities in the spectral region assigned to aliphatic groups (287.8 eV) and the broad shape-resonance centered at 292 eV. After 4 weeks contact with Eu(III), dark and light zones still exhibit these same spectral characteristics (**d**, **f**). Fresh and aged samples after Eu(III)-complexation do not show any morphologies or associated spectra resembling those from the unloaded HA.

Conclusions: NEXFAS curve fitting and analysis of difference spectra unambiguously show an intensity reduction in the energy region around 287.8 eV (3) for the low pH aggregate and the light zones of the fresh humate compared to the spectra of the dark zones. If the common peak assignments are applicable, one may conclude that the dark aggregates possess higher amounts of aliphatic groups. However, as the spectrum of the unloaded HA cannot be reproduced from a superposition of any spectra extracted from the segregated fractions, a distinct complexation effect on the molecular states, damping the strong carboxylate π^* -transition as well as the resonances associated with aromatic carbon, must be inferred. The macromolecular rearrangement detected by STXM suggests it is important to consider conformational changes in humate complex stability as well.

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References: M. Plaschke, J. Rothe, T. Schäfer, M.A. Denecke, K. Dardenne, S. Pompe and K.-H. Heise, "Combined AFM and STXM in situ study of the influence of Eu(III) on the agglomeration of humic acid," *Colloids and Surfaces A*, **197**, 245-256. J. Rothe, M. Plaschke and M.A. Denecke, "Soft X-ray Spectro-Microscopy Investigation of the Formation and Ageing of Eu(III)-induced Humic Acid Aggregates," *Journal de Physique IV* (submitted).



C 1s-NEXAFS spectra obtained from HA aggregates at pH 4.3 (**a**) and after loading with Eu(III)-cations (**b-f**).